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博士（理学）

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学 位 論 文 題 名

Controlled Synthesis of Two-Dimensional Transition Metal Disulfide Monolayers for Solar-Driven Hydrogen Production

(二次元遷移金属硫化物単層の制御合成と光照射下における水素生成助触媒特性)

The production of hydrogen fuels by using sunlight is an attractive and sustainable solution to the global energy and environmental problems. Although platinum (Pt) is known as the most efficient cocatalyst in hydrogen evolution reaction (HER), its high-cost and limited-reserve urge to seek for the alternative non-precious cocatalysts with low-cost and high efficiency. Monolayer transition metal disulfides (TMDs) including molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) are regarded as promising HER candidates to replace Pt due to their highly active edge sites for hydrogen adsorption ($\Delta G_{\text{H}} \sim 0.08 \text{ eV}$) and large in-plane electron mobilities ($>200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). However, until now, facile and efficient preparation of TMDs monolayers has faced with great challenges. Furthermore, the inert but thermodynamically favorable basal planes significantly limit their efficiency in photocatalytic HER. Thus, this thesis focused on targeted synthesis of TMDs monolayers with various phases, lateral sizes, crystallinities, and atomic structures to create more exposed active sites, in particular reactivate the inert basal plane towards superior cocatalytic performance for photocatalytic HER.

In chapter 1, a general background of photocatalytic H_2 evolution, cocatalyst, and transition metal disulfides is introduced. Then, the current strategies to modify transition metal disulfides as efficient cocatalysts are summarized.

In chapter 2, targeted synthesis of semiconductor phase (2H) and metal phase (1T) MoS_2 monolayers was investigated. A facile and effective lithium molten salt assisted method was first developed to synthesize a series of MoS_2 precursors by simply controlling the calcination temperature. These precursors can be easily and accurately exfoliated into 2H- and 1T-phase MoS_2 monolayers by subsequent hydrolysis process. During the synthesis process, lithium molten salt not only acts as the fluxing medium, but also controls the MoS_2 phases switching between 1T and 2H. Due to metallic characteristic, the 1T- MoS_2 monolayers show significantly higher activities than the semiconducting 2H- MoS_2 monolayers over TiO_2 for photocatalytic H_2 evolution.

In chapter 3, a novel strategy through engineering lateral size of TMDs (MoS_2 and WS_2) was explored

for direct exfoliation in polar micromolecular solvents to produce monolayer MoS₂ and WS₂ nanosheets in high yield. The exfoliation yield of monolayers was measured to be as high as 21% for MoS₂ and 18% for WS₂ in ethanol. Even in pure water, a monolayer yield of 6% for MoS₂ and 5% for WS₂ can be achieved. The successful exfoliation of the as-prepared crystals was attributed to the significantly improved ratio of hydrodynamic forces to interlayer van der Waals forces, allowing for ready exfoliation in polar micromolecular solvents. These exfoliated monolayer TMDs nanosheets exhibit superior catalytic H₂ activity when loaded on CdS for photocatalytic HER with optimized sacrificial agents, PH values, and loading amount.

In chapter 4, to further create more active sites in MoS₂ monolayers for triggering a higher HER activity, crystallinity engineering was adopted to enhance its catalytic H₂ activity. It was found that the cocatalytic performance of the monolayer MoS₂ is gradually enhanced with reduced crystallinity, and an apparent quantum efficiency as high as 71.6% can be achieved for the lowest crystalline monolayer MoS₂ over CdS under visible light irradiation at 420 nm. As compared to the highly crystalline monolayer MoS₂, the increased catalytic H₂ activity for the poorly crystalline monolayers is attributed to the low-crystallization induced structural disorder, which contains abundant unsaturated sulfur atoms as additional active sites for HER.

In chapter 5, to effectively reactivate the inert basal plane of MoS₂ monolayers, elemental (like cobalt) doping combining with crystallinity engineering was systematically investigated. The density functional theory calculations and experimental results show that the combination of crystallinity engineering with cobalt substitution can activate and reuse of the inert basal plane of MoS₂ monolayers for HER, leading to the significantly enhanced catalytic H₂ activity with an apparent quantum efficiency of 80.2% over CdS under visible light irradiation at 420 nm.

In chapter 6, an overall summary of this dissertation work was provided. This thesis carried out a systematic study on controllable synthesis of monolayer TMDs and rational design of their active sites for efficient photocatalytic H₂ evolution. By lithium molten salt assisted and edge engineering methods, direct exfoliation and targeted synthesis of 2H-, 1T-phase MoS₂ monolayers can be achieved. By crystallinity engineering, abundant unsaturated sulfur atoms as additional active sites were introduced as an effective way for improving the cocatalytic performance of MoS₂ monolayers. By cobalt doping, the inert basal plane was activated, further enhancing the cocatalytic performance of crystallinity engineered MoS₂ monolayers for photocatalytic HER. This study potentially provides new avenues for facile synthesis and design of more efficient monolayer TMDs cocatalysts for photocatalytic H₂ evolution in the future research.